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Methods of estimations of the band gap for kesterite $Cu_2ZnSnS(Se)_4$

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Abstract

This paper presents a study related to methods of estimation of the band gap for kesterite-type $Cu_2ZnSnS(Se)_4$ based on their electronic structure and optical properties driven by the first-principles calculations within the hybrid functional. The estimations have been performed by four different methods. The first one is based on the band structure estimated as the difference of the energy corresponding to the conduction band and valence band edges. The rest three methods are based on the spectral distribution of the absorption coefficient $\alpha(\hbar\omega)$ driven from the first-principles calculations: (i) Tauc plot, (ii) first derivative of $\alpha(\hbar\omega)$ on photon energy $\hbar\omega$ in the energy range around the fundamental absorption edge, and (iii) linear combination of the methods (i) and (ii). We show that the band gap estimated by different methods can deviate each from other drastically and the large difference is not only relayed to defects, impurities and other lattice imperfections. We show also, that the influence of lattice anisotropy on optical properties of CZTS and CZTSe is negligible. We have pointed out importance of the dependence of dielectric constant on surface texture. The equation describing dependence of dielectric constant on the experimentally observed surface texture is derived.

Keywords: Kesterite-type Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$, band gap, hybrid functional.

1. Introduction

Band gap (Eg) is one of the important parameters characterizing semiconductors. At present there exist several methods of estimations of it from the experimental measurements such as, e.g., X-ray photoelectron spectroscopy [1], temperature-dependent Seebeck coefficient [2], photoacoustic spectroscopy [3], etc. The frequently used one is Tauc method, which is based on analysis of the spectral distribution of the absorption coefficient $\alpha(\hbar\omega)$ [4] and plotting of $(\alpha\hbar\omega)^m$ spectra against photon energy with m=2 for allowed direct band gap and m=1/2 for allowed indirect band gap. Here $\hbar$ is the Plank constant and ω is the photon frequency. The dependence of $(\alpha\hbar\omega)^m$ on photon energy will be analysed around the fundamental absorption edge and approximated by a straight line. Then, one estimates the Eg from intersection of the linear fit with abscissa. Although the method is extensively used, there remain some questions about its accuracy. For example, because of the influence of lattice imperfections, accuracy of the measurement, etc., the dependence $(\alpha\hbar\omega)^m$ on $\hbar\omega$ does not exhibit a well-defined region that can be approximated by a straight line. The other approach developed in Ref. [5] allows to find the band gap as the photon energy $\hbar\omega$ corresponding to the maximum of the derivative of α with respect to $\hbar\omega$ $[d\alpha/d(\hbar\omega)]$ in the range of the photon energies in close vicinity to the fundamental absorption edge. The third method is proposed in Ref. [6]. It suggests plotting the linear approximation of $(\alpha\hbar\omega)^m$ on energy $\hbar\omega$ that passes through $\hbar\omega=E_1$ at which $d\alpha/d(\hbar\omega)=0$ and intersects abscissa at the energy E_2. Then, the band gap can be estimated as the linear combination of E_1 and E_2 according to

$$E_g = (3E_1 + E_2)/4. \quad (1)$$

In practice, the band gaps estimated by using the spectral distribution of the absorption coefficient $\alpha(\hbar\omega)$ within the above-mentioned three ways might show a large scatter and the question as to whether the scatter is because of the method used in the band gap estimation or is it because of the other reasons such as, e.g., lattice imperfections, is an important question. Estimations [7] of the band gap for the F-doped and Sn-doped In_2O_3 within the above mentioned methods differ each from other to ~0.2 eV. Depending on accuracy of the measurement and purity of the material the scatter can be more than 0.2 eV also. This indicates that care should be taken upon selection of the proper method of estimation of the band gap. The question also is which of the methods is the most accurate. One of the ways to clarify it is study of both the band gap E_g and $\alpha(\hbar\omega)$ within first-principles calculations. Then, by using the calculated $\alpha(\hbar\omega)$, estimate the band gap within the rest three methods and compare them with each other. The aim of this paper is study of the problem for kesterite-type $Cu_2ZnSnS(Se)_4$ (CZTS(Se)) that are one of the complicated and popular materials in modern photovoltaic technology [8-12]. Band gap and optical properties of CZTS(Se) have been driven from the first-principles calculations from both band structure and from the theoretically calculated dependence $\alpha(\hbar\omega)$.

2. Motivation for selection of the materials

CZTS(Se) are quaternary compounds. Depending on the synthesis method and thermal processing, different types of structural imperfections can be formed such as the secondary phases, defects, etc. that influence on the band gap. Band gap for CZTS and CZTSe has been studied systematically by both theoretical and experimental methods.

The theoretically estimated bad gap from the first principles calculations by different authors shows large scatter and it depends on the approximations used. The problem becomes more crucial upon considering complicated materials such as CZTS(Se). E_g can be zero or negative within the local density approximation (LDA) and generalized gradient approximation (GGA) [13, 14]. For zinc blende-kesterite CZTS it is reported [15] to be 0.86 eV within the GGA+*U*, be 1.06 eV within sX-LDA [14], and 1.65 eV within PBE+U+G^0W^0 [16]. By the self-consistent GW calculations the band gaps of 1.33 eV and 0.87 eV have been reported [15] for stannite CZTS and CZTSe as well as 1.64 and 1.02 eV for kesterite. One of the accurate and time consuming approximations is hybrid functional calculations. However, that requires knowledge of a parameter called "range separated parameter" and the calculated band gap depends on it.

The experimentally determined band gap for the kesterite-type CZTS and CZTSe also shows large scatter between 1.3-1.7 eV [17, 18] and 0.8-1.6 [19], respectively. Cu-Zn disorder is reported [20] to play critical role in band gap fluctuations of CZTS. Possibility of tuning the band gap between 1.0 and 1.5 eV is reported [12] by increasing the S/Se ratio in CZTS. Possibility of band gap engineering has been reported [21] because of influence of the secondary phases of Cu_2S and SnS. So, especially in such compounds like CZTS(Se) analysis of capabilities of different methods of estimating the band gap for these materials is an important task.

3. Methods

Structural optimization, electronic structure and optical properties for CZTS(Se) have been studied by the Vienna ab initio simulation package (VASP) [22, 23] together with the potential projector augmented-wave (PAW) method [24, 25]. Exchange and correlation effects have been described by the Perdew-Burke-Ernzerhoff (PBE) [26] of generalized gradient approximation (GGA) as well as HSE06 hybrid functional containing a modified portion of the Fock exchange. PAW-PBE pseudopotentials were employed to describe the Cu($4s^13d^{10}$), Zn($3d^{10}$,$4s^2$), Sn($4d^{10}5s^25p^2$), S($3s^23p^4$), and Se ($3d^{10}4s^24p^4$) valence states. Hybrid functional was performed as the proposed by Heyd-Scuseria-Ernzerhof (HSE) [27]. The screening parameter and Hartree-Fock exchange part has been taken as 0.25 $Å^{-1}$ and 25%, respectively. Structural optimization was performed with k-mesh 8x8x8, plane-wave cut-off energy 600 eV, and energy error 10^{-8} eV. The residual forces and pressure are less than 10^{-4} eV/Å and 0.06 kB, respectively. Electronic structure calculations have been performed that were used for estimations of the band gap E_g. Imaginary and real parts of the macroscopic dielectric function have been calculated that were used for estimation of absorption coefficient α as a function of the photon energy $\hbar\omega$ in the 0-10 eV energy range.

4. Results

4.1 Band gap from band structure calculations

Full optimization of the lattice has been performed within both CZTS and CZTSe within PBE and hybrid functional approximations. Lattice parameters optimized by hybrid functional better agrees with experimental data. Then, electronic structure calculations have been performed. Calculated total density of states (DOS) agrees well with X-ray photoelectron spectroscopy measurements [Supplementary information]. By analysis of the orbital and site

projected DOS, the origin of the bands in the valence and conduction bands have been clarified. The results agree well with the results documented in literature on electronic structure studies.

Band gap for CZTS and CZTSe has been estimated as the difference of the energy corresponding to the topmost valence band from the bottommost conduction band from ab initio calculations of electronic structure. According to the calculations within GGA the band gap is zero for both CZTS and CZTSe. Upon performing the electronic structure studies with hi accuracy, the band gap becomes slightly larger than the band gap. Then, the wavefunction generated from the PBE calculations have been used for electronic structure within hybrid functional approximations. Table I presents the theoretical results as compared to the experimentally established ones. Analysis shows that the band gap calculated within HSE06 hybrid potential agree well with the experimentally established band gap. The HSE06 results will be used for comparing the band gaps estimated from $\alpha(\hbar\omega)$ within the above mentioned three methods.

Table I. *Fundamental band gap E_g (eV) for CZTS(Se) calculated within PBE and HSE06 from electronic structure studies and from $\alpha(\hbar\omega)$ within three approaches as compared to experimental data.*

Method	CZTS	CZTSe
PBE	0.00	0.00
HSE06	1.49	0.90
Tauc [ ]	1.35	0.71
Hamberg et.al. [ ]	1.33	0.68
Roth at.al. [ ]	1.30	0.61
Expt.	(1.3-1.7)[a]	(0.8-1.6)[b]

[a)]Experiment [17, 18].

[b)]Experiment [19].

4.2 Influence of lattice anisotropy and surface texturization on optical properties of CZTS(Se)

Lattice anisotropy and surface texturization also strongly influences on optical properties of materials. In the band gaps estimated from the experimentally measured $\alpha(\hbar\omega)$, influence of these points are already included. Since in this work we calculate $\alpha(\hbar\omega)$ from first principles calculations within hybrid functional, the influence of the lattice anisotropy and surface texturization on optical properties of CZTS(Se) is not included and we should evaluate how strong is the influence. Imaginary and real parts of the macroscopic dielectric function have been calculated along E⊥c and E||c directions that are expected to differ each from other because of the anisotropy of the lattice. Our study within hybrid functional showed that the difference is negligible in the photon energy ranges of solar light.

During synthesis of CZTS(Se) texturing of the surface can take place along the direction (112) (see, e.g., Ref. [28]). That will influence on magnitude of the dielectric constant of CZTS(Se). To account for the influence of texturing of the surface of CZTS(Se), we have derived the dependence of dielectric constant on directions. Since the dielectric constant is the tensor of second order and for tetragonal lattice when the piezoelectric properties are not accounted for, it has the form of diagonal matrix, the formulation for ε can be written as:

$$\varepsilon_{(112)} = e_1^2\varepsilon_{11} + e_2^2\varepsilon_{22} + e_3^2\varepsilon_{33}, \quad (2)$$

where e_1, e_2, and e_3 are the cosine of the direction for (112)-plane normal; ε_{11}, ε_{22}, ε_{33} are the corresponding tensor elements of the dielectric constant. Here ε_{11} and ε_{22} correspond to E⊥c and ε_{33} – E||c, respectively. Determining the normal through the vector of the reciprocal lattice, one can get:

$$\boldsymbol{e_1 = e_2 = \frac{c}{\sqrt{2c^2+4a^2}} = 0.5774;\ e_3 = \frac{2a}{\sqrt{2c^2+4a^2}} = 0.5773.} \quad (3)$$

By substituting the formulations for e_1, e_2, and e_3 (Eq. (3)) into Eq. (2) and accounting for the Eq. $\varepsilon_{11} = \varepsilon_{22}$, which is valid for tetragonal lattice, one can get the formulation for the dielectric constant for CZTS textured along (112)

$$\varepsilon_{(112)} = 0.6667\varepsilon_{11} + 0.3333\varepsilon_{33}. \quad (4)$$

In this work, we have first calculated real and imaginary part of permittivity tensor for different energies by first-principles studies within hybrid functional. To account for the influence of surface texturization, ε_1 and ε_2 spectra have then been estimated according to Eq. (4) as a linear combination of the corresponding tensor elements.

4.3 Band gap from spectral distribution of absorption coefficient

We have calculated $\alpha(\hbar\omega)$ using the ε_1 and ε_2 for CZTS(Se) from first principles calculations within hybrid functional and them updated them according to Eq. (4). The updated $\alpha(\hbar\omega)$ was used to estimate the band gap

according to Tauc plot, first derivative of $\alpha(\hbar\omega)$ on $\hbar\omega$ in the photon energy range around fundamental absorption edge, and according to Eq. (1). The results are displayed in Fig. 1 (a)-(c). The band gaps estimated from the fittings are presented in Table I. Although the difference between the band gaps 1.35 eV, 1.33, and 1.30 estimated for CZTS by the three methods is < 4%, they differ from 1.49 eV calculated by hybrid functional to 9%, 11%, and 13%, respectively. The band gaps calculated for CZTSe 0.71 eV, 0.68 eV, and 0.61 eV differ each from other by less than 16%. However, they differ from 0.90 eV estimated from band structure to 21%, 24%, and 32%, respectively. The difference of the band gaps of CZTS(Se) based on band structure calculations from that based on $\alpha(\hbar\omega)$ can be explained by accuracy of estimation of optical matrix elements by DFT [29]. Since we have studied defect free CZTS(Se), the large difference in the calculated band gaps can be related to the method of estimation. Defects, impurities or other lattice imperfections cannot be the only reasons for discrepancy of the calculated band gaps.

5. Conclusions

We have studied band gap and optical properties for CZTS and CZTSe by first principles calculations within PBE and hybrid functional approximations. The band gaps estimated from band structure have been compared to those evaluated from Tauc plot, first derivative of $\alpha(\hbar\omega)$ on $\hbar\omega$ in the photon energy range around fundamental absorption edge, and linear combination of Tauc plot with extremum in the dependence $\alpha(\hbar\omega)$ according to Eq. (1). The difference between the band gaps 1.35 eV, 1.33, and 1.30 estimated for CZTS from $\alpha(\hbar\omega)$ is found to be less than 4%. However, these band gaps differ from 1.49 eV calculated from band structure to 9%, 11%, and 13%, respectively. The band gaps for CZTSe 0.71 eV, 0.68 eV, and 0.61 eV estimated from $\alpha(\hbar\omega)$ differ each from other by less than 16%. However, they differ from 0.90 eV estimated from band structure to 21%, 24%, and 32%, respectively. The analysis showed that the large difference in the estimated band gaps by different methods cannot always be ascribed to defects, impurities or other lattice imperfections. It can be related to method of estimation as well. To improve accuracy of estimation of absorption coefficient, we have studied dependence of absorption coefficient on lattice anisotropy, which is found to be negligible. Influence of surface texturization on optical properties has been accounted for by deriving the formulation for the dielectric constant for the experimentally observed texturing of CZTS along the direction (112).

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Figure captions

Figure 1. Estimation of the direct band gap for CZTS(Se) from (a) Tauc plot, and methods suggested by (b) Hamberg et.al. [5] and (c) Roth et.al.[6].